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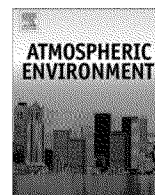Project   NHEXAS-Maryland Longitudinal Exposure Investigation View project

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Modeling the air–soil transport pathway of perfluorooctanoic acid in the mid-Ohio Valley using linked air dispersion and vadose zone models

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article info

abstract

As part of an extensive modeling effort on the air–soil-groundwater transport pathway of per-fluorooctanoic acid (PFOA), this study was designed to compare the performance of different air dispersion modeling systems (AERMOD vs. ISCST3), and different approaches to handling incomplete meteorological data using a data set with substantial soil measurements and a well characterized point source for air emissions. Two of the most commonly used EPA air dispersion models, AERMOD and ISCST3, were linked with the EPA vadose zone model PRZM-3. Predicted deposition rates from the air dispersion model were used as input values for the vadose zone model to estimate soil concentrations of PFOA at different depths. We applied 34 years of meteorological data including hourly surface measurements from Parkersburg Airport and 5 years of onsite wind direction and speed to the air dispersion models. We compared offsite measured soil concentrations to predictions made for the cor-responding sampling depths, focusing on soil rather than air measurements because the offsite soil samples were less likely to be influenced by short-term variability in emission rates and meteorological conditions. PFOA concentrations in surface soil (0e30 cm depth) were under-predicted and those in subsurface soil (>30 cm depth) were over-predicted compared to observed concentrations by both linked air and vadose zone model. Overall, the simulated values from the linked modeling system were positively correlated with those observed in surface soil (Spearman's rho, R_{sp} ¼ 0.59e0.70) and subsur-face soil (R_{sp} ¼ 0.46e0.48). This approach provides a useful modeling scheme for similar exposure and risk analyses where the air–soil-groundwater transport is a primary contamination pathway.

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1. Introduction

Ammonium perfluorooctanoate (APFO) is one of the major environmental contaminants of concern in the United States, and its use is growing worldwide. APFO has been used as a surfactant in the manufacture of Teflon[ffl] and other fluoropolymers by the DuPont Washington Works Facility in Parkersburg, West Virginia, since the early 1950s. There are extensive ongoing efforts to understand past, present, and future levels of APFO contamination surrounding that specific site (Paustenbach et al., 2007; DuPont, 2008; Shin et al., 2011a). APFO is of recent concern to toxicologists and epidemiologists due to potential liver toxicity, tumorige-nicity, dislipidemia, immunotoxicity, and developmental effects (Steenland et al., 2010). Animal studies showed several toxic effects of APFO (Abdellatif et al., 1991; Nilsson et al., 1991; Kennedy et al., 2004; Luebker et al., 2005; Lau et al. 2006, 2007), but little infor-mation is available for human health effects of APFO (Steenland et al., 2010). Due to potential adverse health effects, the presence of dissociated APFO in local water supplies has motivated the study of human exposures for residents living near the facility (Emmett et al., 2006; Frisbee et al., 2009; Steenland et al., 2009; Shin et al., 2011b).

APFO is a white solid at ambient temperature, but exists as a vapor when it exits the hot dryer of the facility. When the hot APFO vapor exits through stacks, it tends to condense to form

fumes which consist of fine particulates (Seidel et al., 1991; Mendez et al., 2000; Oberdorster et al., 2000). Within several minutes in ambient environments, it coagulates and forms micron-sized particulates ranging from 0.1 to 1 mm in aerodynamic diameter (U.S. EPA, 1990; Seidel et al., 1991; Flagan, 1994; Oberdorster et al., 2000). APFO in a particulate phase is transported to nearby public well fields by wind and is deposited onto the surface of overlying well fields by dry and wet deposition (Davis et al., 2007). When deposited APFO, the undissociated salt form, is in aqueous phase, it dissociates into perfluorooctanoate (PFO$^-$) and ammonium ion (NH$_4^+$). In acidic environments, PFO$^-$ is protonated to form perfluorooctanoic acid (PFOA). Thus, the ratio of PFO$^-$/PFOA is determined based on reported pKa and environmental pH. The reported pKa value of PFOA ranges from 0 to 3.8 (Kissa, 2001; Prevedouros et al., 2006; Burns et al., 2008; Goss, 2008). PFO$^-$ will be dominant in most water bodies and soils since typical environmental pH exceeds 4. PFO$^-$ is also a dominant form both in surface soil and in subsurface soil of this model domain as pH is between 4 and 7 (Collier, 1984). However, the term 'PFOA' is used to describe environmental measurements of the sum of PFO$^-$ and PFOA in the present study to be consistent with other literature.

One of the major reported routes of APFO from the DuPont Washington Works Facility to the local environment is through air emission stacks (Paustenbach et al., 2007). There was a 99% decline in PFOA atmospheric releases from the facility between 2000 and 2006, but high PFOA concentrations have been detected in offsite surface and subsurface soil in 2005 and 2006 (DuPont, 2008), suggesting substantial retardation of vertical transport through the soil. PFOA air e soil transport is considered an important pathway as the highest soil concentrations are measured upstream and downwind of the facility. Davis et al. also supported that PFOA air transport to the surface soils of nearby water supplies located upstream of the facility resulted from wet deposition of air emissions during rain events because groundwater transport was highly unlikely based on the groundwater capture zones (2007).

DuPont conducted an air modeling and monitoring comparison study using AERMOD and ISCST3, two of the most commonly used air dispersion models (DuPont, 2007; US EPA, 1995, 2004). They reported that AERMOD predicts air concentrations better than ISCST3 for both off-site and on-site meteorological data due to improved AERMOD functions for dealing with boundary layer conditions and stability class (DuPont, 2007; Barton et al., 2010). However, there were several limitations to this study. First, sampling dates were randomly chosen within a short period of time, but annual emission rates were used to model short term predictions. Second, 1999 onsite meteorological data were used to predict deposition patterns for September and October 2005, and January 2006. Third, model predictions were compared to concentrations from surface soil/grass samples taken at a depth < 2.5 cm although PFOA within this shallow depth could be quickly swept away by runoff in a short period of time or disappear by removal mechanisms that occur in soil such as plant uptake, evaporation, irrigation, and erosion. In contrast, PFOA concentrations in subsurface soil result from fate and transport over longer time scales with more dispersive mixing, and should therefore be less sensitive to short-term variations in source emissions and meteorology.

The present study addresses several limitations of earlier air dispersion modeling efforts. In particular, well-integrated meteorological data is important to use in the prediction of PFOA deposition because wind direction and speed are important parameters of determining the shape and size of dispersion, and precipitation rate accelerates wet deposition near the direct sources of emissions. Therefore, several meteorological data sets were carefully integrated for use in AERMOD and ISCST3 using the nearest airport (i.e., Parkersburg) data. In addition, we also incorporated the

vadose zone model PRZM-3 to simulate the fate and transport of PFOA in surface and subsurface soil, allowing direct comparison with observed soil concentrations.

The objective of our study was to evaluate the linked air e soil model as a predictive tool for the fate and transport of PFOA from the source through atmosphere to the vadose zone by comparing observed and predicted surface and subsurface soil concentrations. We also compared predictions from AERMOD and ISCST3 models and investigated the sensitivity of our results to different approaches for meteorological data processing.

2. Materials and methods

2.1. Sampling data

In this study, we used offsite surface (0 e 30 cm depth) and subsurface (> 30 cm depth) soil samples collected within our air dispersion model domain (Fig. 1) to evaluate the performance of the linked air and vadose zone model by comparing with predicted PFOA concentrations in surface and subsurface soil. A total of 232 surface soil samples were collected previously from 32 locations in August 2002, September and October 2005, and April 2006 (DuPont, 2008). The sample concentrations for each location were averaged for each year. In addition, 242 subsurface soil samples from 10 locations were collected in August 2002 and March and April 2006. There were 12 to 34 subsurface soil samples of varying depth collected at each sampling location. Onsite soil samples that had PFOA concentrations two to four times higher than offsite samples were not included in this analysis because other pathways including the leaching from onsite contaminated anaerobic digestion ponds or landfill may be involved and the large surface area of the facility is covered by pavement. Rationale for selecting sample locations, sampling procedures, and analytical methods for soil samples are described in detail elsewhere (DuPont, 2005; Barton et al., 2010).

2.2. Air dispersion model

2.2.1. Model description

We chose to compare the U.S. EPA Industrial Source Complex Short Term version 3 (ISCST3) model (US EPA, 1995) and the American Meteorological Society/EPA Regulatory Model (AERMOD) (US EPA, 2004) because these models characterize atmospheric dispersion of chemicals well and have been recommended by EPA. Both models are similar in that they use a steady-state Gaussian plume model that predicts the ambient air concentrations and deposition rates at geographical locations defined as receptors, but AERMOD determines the vertical and horizontal dimensions of plumes by type of stability class (US EPA, 2004). A detailed comparison of model features for ISCST3 and AERMOD has been published elsewhere (US EPA, 2003). EPA recommended AERMOD over ISCST3 for regulatory purposes in 2005 (US EPA, 2004). ISC-AERMOD view, graphical interface software, was also used to generate input files for multi-year simulations (Lakes Environmental, Waterloo, Ontario, Canada).

2.2.2. Input parameters

We relied on most of the model input parameters provided by Paustenbach et al. (2007). These parameters include building configuration, stack information, emission rate, and particle size. Building dimension information for the facilities was included in the model to account for the effect of building downwash (U.S. EPA, 1995). Historical stack information such as height, diameter, exit velocity, and temperature was applied to the model by source and year. The procedure of material mass balance to estimate historical air emission rates for the period 1951 e 2003 is described in detail in
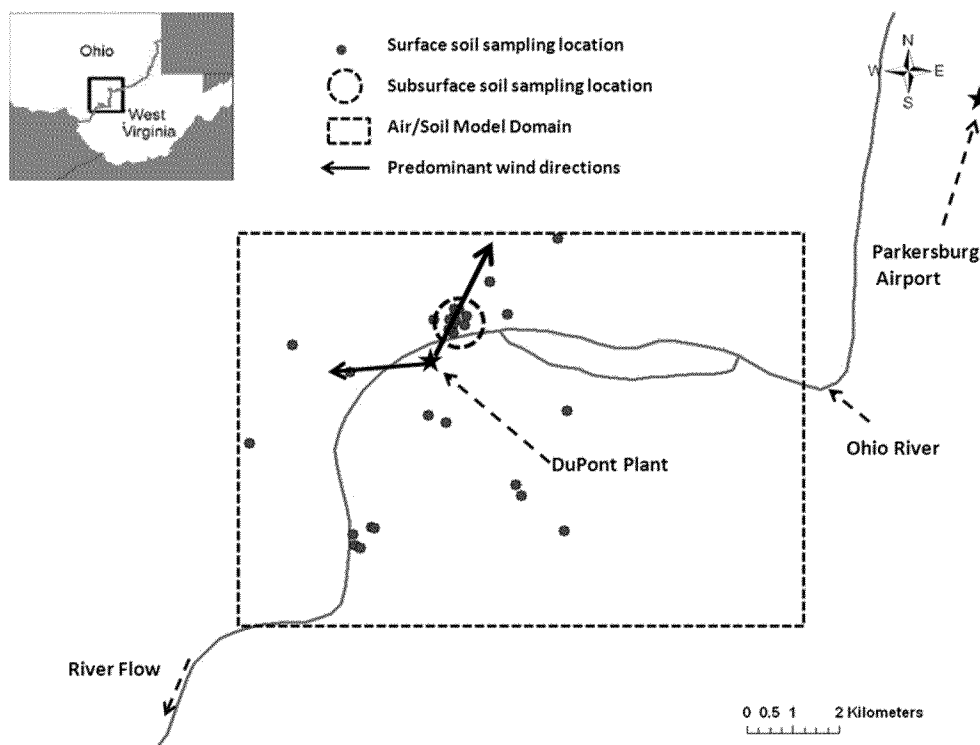
Fig. 1. Study area, surface and subsurface soil sampling locations, and air/soil model domain (dotted box). Surface soil sampling locations are shown as points and subsurface soil sampling locations are clustered in a dotted circle. Solid lines represent predominant wind directions near DuPont Plant. Parkersburg Airport wind directions are more evenly distributed.

Paustenbach et al. Total emissions estimates for 2004, 2005, and 2006 were estimated from a figure provided by DuPont, assuming that all manufacturing processes that operated in 2003 were still in operation through 2006 (DuPont, 2008). We assumed that the predominant physical state in the atmosphere is micron-sized particulates of APFO as explained in the Introduction. Thus, we applied particle density and different particle size categories of APFO found in the fence line of the DuPont Washington Works Facility (Barton et al., 2007) and in the exit stream of different industrial processes (DuPont, 2008) to the air dispersion models (ISCST3 and AERMOD). We describe particle size information in detail in the Appendix. Raw particle size data with 12 categories, also provided by DuPont (2007), was applied to the model instead of using five collapsed particle size categories used by Paustenbach et al. WebGIS was used to download additional terrain elevation information and to assign terrain elevation to each model grid point, also referred to as a receptor. A Cartesian coordinate system was used to make the grid array with a spacing of 200 meters and the coordinates of the model domain origin were set as 437,800 and 4,341,000 meters. Paustenbach et al. provided five years (1996, 1999, 2000, 2001, and 2002) of onsite meteorological data that could be only compiled by the ISCST3. We combined onsite wind direction and speed with offsite surface characteristics measured at the Parkersburg Airport (WV) and precipitation rates measured in Liverpool, WV, to account for the different patterns of wind direction and speed at the facility compared to the Parkersburg Airport. We describe different approaches to handling incomplete meteorological data for ISCST3 and AERMOD in detail in the Appendix.

2.3. Vadose zone model

2.3.1. Model description
    U.S. EPA Pesticide Root Zone Model Version3 (PRZM-3) was developed to predict soil concentrations in the vadose zone (U.S.

EPA, 2005). PRZM-3, a one-dimensional, dynamic compartment model, simulates pesticide transport from the ground surface through the vadose zone. PRZM-3 has two distinct modules; PRZM and VADOFT. The former is a one-dimensional, finite-difference model that accounts for pesticide and nitrogen fate in the crop surface zone (0e30 cm depth) whereas the latter is a one-dimensional, finite-element code that solves the Richard's equation for flow in the vadose zone (>30 cm depth). The VADOFT module was set up with 51 nodes to model the transport of PFOA at all different depths ranging from about 30 cm to 1,800 cm. Both PRZM and VADOFT have two model components e hydrology and chemical transport. The hydrologic component calculates runoff and erosion. Water movement is simulated based on the generalized soil parameters, including field capacity, wilting point, and saturation water content. The chemical transport component can simulate the fate and transport of pesticide after its application on the soil or on the plant foliage. The process of biodegradation is modeled in the root zone. Dissolved, adsorbed, and vapor-phase concentrations in the soil are simulated by simultaneously considering the processes of pesticide uptake by plants, surface runoff and erosion, decay/transformation, volatilization, advection, dispersion, and retardation/sorption (U.S. EPA, 2005).

2.3.2. Input parameters
    We ran PRZM-3 in a dynamic mode, with hourly rainfall and time-variable flow with varying water content. We applied PRZM-3 to the same geographic extent as the air dispersion model using a model cell size of 400 m by 400 m. The PRZM-3 model using the deposition flux from the air dispersion models estimated annual average soil concentrations for different ranges of depth. In addition, the model requires 22 different input parameters including bulk density, organic carbon fraction, porosity, and longitudinal dispersivity. Since these parameters were dependent on a soil type and a hydrologic soil group, a dominant soil type was assigned to

each model cell. Geographic data on each soil type was obtained from the State Soil Geographic (STATSGO) database of the National Resources Conservation Service (NRCS). Predominant soil types in our model domain were silt loam, silt clay loam, and silty clay. A Geographic Information System (GIS) was used to spatially join the STATSGO soil data to the X and Y coordinates of the model cells. Due to limited vertical soil information, soil type was assumed to be constant at all depths within a model cell. The model was independently simulated in each grid cell assuming that lateral transport did not occur across the grid block and vertical transport with rainfall recharge was dominant within grid blocks. Soil column thickness between ground surface and groundwater table was computed using the difference between average cell elevation and average cell groundwater head of the groundwater flow model developed by DuPont (2003).

2.3.3. Input chemical properties of PFOA

PFO^{-} is the conjugate base of PFOA and the ratio of PFO^{-}/PFOA in aqueous solution is strongly pH-dependent. Thus, chemical properties of an acid-base pair (i.e. PFOA-PFO^{-}) should be estimated in terms of a distribution ratio (D_{ij}) of an organic acid or base i and a property j (Schwarzenbach et al., 2003). For example, the octanolewater distribution ratio of the PFOA-PFO^{-} pair ($D_{PFOA,ow}$) is pH dependent from the following equation (Schwarzenbach et al., 2003).

$$D_{PFOA;ow} = \frac{[PFOA]_{o;tot}}{[PFOA]_{w} + [PFO^{-}]_{w}} \qquad (1)$$

where $[PFOA]_{o,tot}$ is the total concentration of PFOA in octanol, $[PFOA]_{w}$ the concentration of PFOA in water, and $[PFO^{-}]_{w}$ the concentration of PFO^{-} in water. Therefore, the chemical properties of the PFOA-PFO^{-} pair, which are a function of environmental pH including vapor pressure, solubility, airewater distribution coefficient ($D_{i,aw}$), and octanolewater distribution coefficient ($D_{i,ow}$), need to be presented as the distribution ratios (D_{ij}).

Partitioning behavior of the dominant species, PFO^{-}, in soil and water is strongly determined by the soilewater partition coefficient (K_d) (Schwarzenbach et al., 2003). The value of K_d can be estimated by either a function of the octanolewater partitioning coefficient (K_{ow}) or the product of the organic-carbon partitioning coefficient (K_{oc}) and the organic-carbon fraction in soil (f_{oc}). However, published estimates of the octanolewater distribution ratio (log D_{ow}) (i.e. the same property of K_{ow} for the PFOA-PFO^{-} pair) and the organic-carbon distribution coefficient (log D_{oc}) (i.e. the same property of K_{oc} for the PFOA-PFO^{-} pair) for PFO^{-} vary widely, from 1.2 to 4.3 (Meylan and Howard, 1995; Jing et al., 2009; Rayne and Forest, 2009) and 0.4 to 2.1 L kg^{-1} OC, respectively (Dekleva, 2003; Arp et al., 2006; Higgins and Luthy, 2006; Shin et al., 2011a). There are three potential reasons for these wide ranges. First, its strong tendency to adsorb to surfaces makes experimental determination difficult (Arp et al., 2006). Second, published estimates might be determined in different pH-conditions (Schwarzenbach et al., 2003). Third, the values of PFOA and PFO^{-} were not reported separately. Jing et al. estimated the octanolewater partitioning coefficient (log K_{ow}) of 2.57 for the dissociated ions (i.e. PFO^{-}) using cyclic voltammetry (2009). Rayne and Forest reported both log K_{ow} ranging from 3.6 to 6.3 and log D_{ow} ranging from 1.2 to 4.3 for PFOA from experiments, parameter estimation computer software, and other theoretical methods based on chemical structure (2009). The estimated log K_{ow} for PFOA from an atom/fragment contribution method introduced by Meylan and Howard is 6.3 (1995). Arp et al. predicted log K_{ow} values ranging from 3.6 to 4.3 for PFOA using chemical property estimation software including SPARC, COSMOtherm, ClogP, and EPISUITE (2006). Because the octanolewater partitioning behavior of the PFOA-PFO^{-} pair is pH-dependent, we

used an average value of 2.66 between the log K_{ow} value for PFO^{-} from Jing et al. and D_{ow} values for the PFOA-PFO^{-} pair from Rayne and Forest assuming that pH-conditions from two studies were same.

The estimated organic-carbon partitioning coefficient (log K_{oc}) of 2.1 from Dekleva is for the protonated form, PFOA (2003). Higgins and Luthy reported empirically estimated log K_{oc} of 2.1 for the PFOA-PFO^{-} pair (2006). Armitage et al. (2009) used log K_{oc} of 2.1 assuming that both Dekleva and Higgins and Luthy studies estimated log K_{oc} for PFO^{-} (2009). Under the poor organic-carbon fraction in soil (f_{oc}) in the study area, our previous study reported an optimized log K_{oc} value of 0.4 L kg^{-1} OC of PFO^{-} based on calibration against measured well water concentrations, although we originally used the term PFOA for consistency with other literature (Shin et al., 2011a). We chose the K_{oc} of 108.2 because it was used in the vadose zone model of a previous study in the same region (Paustenbach et al., 2007), and we applied the fraction of organic carbon (f_{oc}) in surface soil of 0.006 and in subsurface soil of 0.002 recommended by EPA (1996).

The airewater partition coefficient (K_{aw}), which characterizes the distribution between gas and dissolved phase in soil, is another important input chemical parameter in PRZM simulations. The estimated K_{aw} value for PFOA from vapor pressure and water solubility listed in Paustenbach et al. (2007) is 8.6×10^{-5}. Another reported K_{aw} value for a neutral form is 0.00102 (Barton et al., 2007). Using the fact that $D_{aw} = a K_{aw}$, where D_{aw} is the airewater distribution coefficient for the PFOA-PFO^{-} pair and a is the fraction of a chemical in the non-dissociated form (Schwarzenbach et al., 2003), the D_{aw} values for the PFOA-PFO^{-} pair can be estimated. Based on the pH range between 4 and 7 in the model domain and pK_a range between 0 and 3.8 of the acid form, the largest fraction of the chemical in the neutral form would be 40% when the pH of water is 4 and pK_a of the chemical is 3.8. Thus, the estimated D_{aw} values for the PFOA-PFO^{-} pair range from 0 to 4.0×10^{-4}. We assumed that chemical loss due to volatilization was negligible as PFO^{-} is highly soluble and can be assumed to have a negligible vapor pressure (Barton et al., 2007). We conducted the sensitivity analysis for a single grid cell by changing D_{aw} values from 1.0×10^{-9} to 1.0×10^{1} and confirmed that the model output was not sensitive to D_{aw} values between 0 and 4.0×10^{-4} (see Fig. A1 in the Appendix). We also assumed that plant uptake, surface runoff and erosion, and decay/transformation were negligible; little information is available on those potential losses from the soil compartment.

2.4. Model evaluation

We ran two different simulations with ISCST3 and AERMOD for PFOA dispersion in air, using meteorological data from Parkersburg Airport and using combined Parkersburg and onsite meteorological data (hybrid), for a total of four simulations. Each simulation was then linked to the PRZM-3 vadose zone model to model PFOA transport through the vadose zone. Predicted surface soil concentrations were extracted from the PRZM module and predicted subsurface soil concentrations from the VADOFT module for different depths.

The performance of each linked model (ISCST3-PRZM-3 or AERMOD-PRZM-3) with two different meteorological data (Parkersburg or hybrid) was summarized by categorizing simulated results as over-prediction, under-prediction, and close approximation. Over prediction is defined as the values greater than 2 times the sampling data, under-prediction as the values smaller than 0.5 times the sampling data, and close-approximation as the values between 0.5 and 2 times the sampling data; Barton et al. applied the same cutoff values for comparisons (2010).

Performance differences were formally assessed using McNemar's exact test applied to the proportions of predictions in the close-approximation category. Spearman's rank correlation coefficient (R_{sp}) was also used to measure the strength of association between predicted and observed soil samples.

3. Results

3.1. Surface soil

The simulations from the two ISCST3 runs provided similar slopes of linear relationship between predicted and observed concentrations (0.66 from ISCST3-Parkersburg and 0.61 from ISCST3-Hybrid). Parkersburg Airport and hybrid meteorological data only differ in wind direction and speed. However, different wind information resulted in very different deposition profiles from AERMOD simulations. Predicted deposition rates from ISCST3 were larger than those from AERMOD using the same meteorological data conditions, demonstrating the difference when boundary layer conditions and stability class are considered.

Annual average predicted and observed surface soil concentrations for 55 sampling locations are shown in log 10 scale in Fig. 2. Results show that on average, PFOA concentrations in surface soil were under-predicted in all simulations based on the points clustered under the 1:1 line. This might be due to the use of roughly estimated annual average air emission rates from a figure provided by DuPont instead of using actual daily emission rates from material mass balance as had been done for years prior to 2004. Table 1 summarizes model performance for surface soil concentrations regarding over-prediction, under-prediction, and close-approximation. The percentage of prediction in the close-approximation category from ISCST3-PRZM-3 simulations was higher than those from AERMOD-PRZM-3 simulations for both

meteorological data sets. For surface soil, ISCST3 predicts soil concentrations better than AERMOD when using Parkersburg meteorological data (p¼0.002), but the difference was not statistically significant for the hybrid meteorological data.

3.2. Subsurface soil

Fig. 3 shows the scatter plot of observed and predicted subsurface soil concentrations in log 10 scale for 10 sampling locations. An average sampling depth was used to extract predicted concentrations equal to the same average sampling depth. All simulations except AERMOD-PRZM-3 with Parkersburg Airport meteorological data over-predicted subsurface soil concentration based on the points clustered above the 1:1 line. Fig. 4 shows the scatter plots of cross-sectional subsurface soil concentration prediction profiles by soil depths (cm). We averaged predicted and observed concentrations across sampling locations. Both Figs. 3 and 4 indicate that predictions from ISCST3-PRZM-3 simulations with both meteorological data sets were not starkly different from the AERMOD-PRZM-3 simulations, with predictions on the correct order of magnitude but generally higher than the observed mean soil concentrations. The peak prediction observed near 800 cm in Fig. 4 is near the contact between the overlying silty clay and the underlying sand and gravel. When PFOA that is transported via rainfall recharge through the soil column of silty clay meets the sand and gravel unit, it is possible that PFOA concentrations were increased due to different soil properties such as porosity or the organic carbon fraction in soil. Performance of model simulations for subsurface soil concentration is summarized in Table 2. R_{sp} for all airesoil simulations does not show much difference in performance among different combinations of simulations. For subsurface soil, differences between the ICSST3 and AERMOD predictions were not statistically significant although AERMOD offered borderline
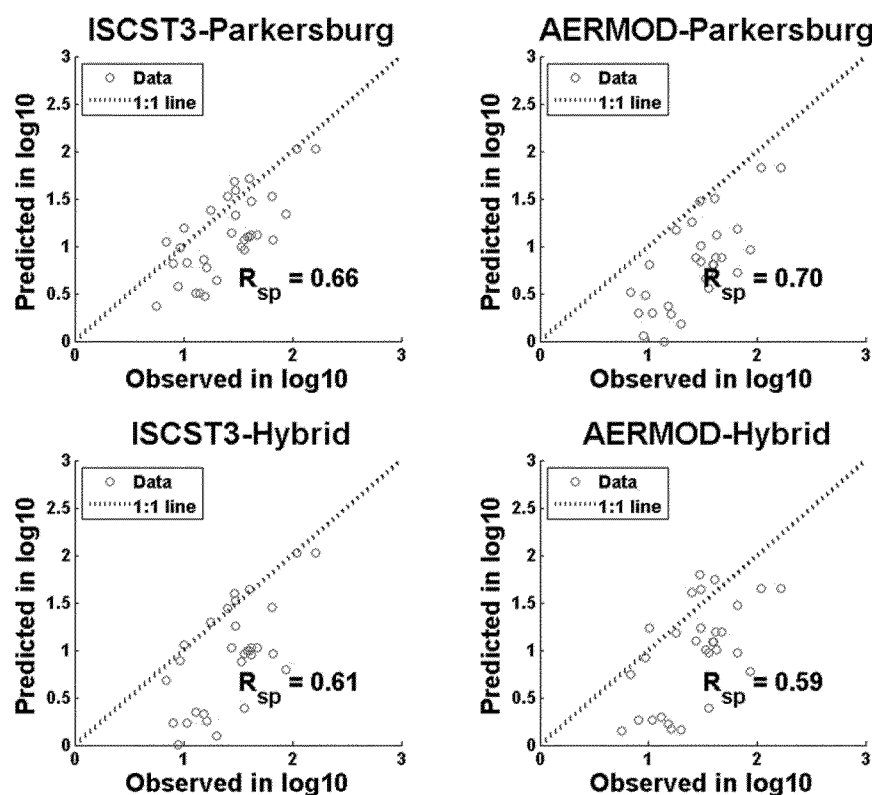

Fig. 2. Linear scatter plots of predicted and observed surface (0e30 cm) soil concentration (mg k g^{-1}). Predicted and observed concentrations are shown as points.

Table 1
Performance of model predictions for surface soil (0e30 cm) concentrations (mg kg^{-1}) by different air dispersion models and meteorological data. R_{sp} represents Spearman's correlation rank coefficient and p-value was computed from the McNemar's exact test.

Air model	Meteorological data source	R_{sp}	Under-prediction		Close-approximation		Over-prediction		p-Value
			n	%	n	%	n	%[a]	
ISCST3	Parkersburg Airport	0.66	17	52	16	48	0	0	0.002
AERMOD		0.70	27	79	6	21	0	0	
ISCST3	Hybrid	0.61	22	67	11	33	0	0	0.25
AERMOD		0.59	24	73	8	24	1	3	

[a] Percentage of predictions in each prediction category defined in Model Evaluation section.

improvement (p¼0.06) compared to ISCST3 for the Parkersburg meteorological data.

4. Discussion

This study was part of a larger effort to estimate retrospective PFOA exposure for participants in the C8 Health Project, a very large and unique cross-sectional study that began in 2005 (Frisbee et al., 2009). People are concerned about exposure to PFOA via not only contaminated agricultural produce, but also drinking water ingestion and air inhalation. A variety of fate and transport studies, epidemiologic studies, regulatory activities, and legal actions are being conducted in this region, whose residents have the highest PFOA serum concentrations ever reported for non-occupational exposures in the US. As part of an extensive modeling effort on the airesoil-groundwater transport pathway of PFOA, this study was designed to compare the performance of different air dispersion modeling systems (AERMOD vs. ISCST3), and different

approaches to handling incomplete meteorological data using a data set with substantial soil measurements and a fairly well characterized point source for air emissions.

Comparison of monitored concentrations with predicted concentrations by soil depth in Fig. 4 allowed us to evaluate the performance of the linked airesoil models on the prediction of PFOA transport through the vadose zone with rainfall recharge. This comparison demonstrated that changes in wind direction and speed did not influence the deposition rate modeled by ISCST3, but did have a small effect on that modeled by AERMOD. We also performed the McNemar's exact test for Parkersburg vs. onsite meteorological data for surface soil and subsurface soil, but found that the choice of meteorological data does not substantially influence the predictions of surface and subsurface soil concentrations for both ISCST3 and AERMOD (similar R_{sp} values and p > 0.05 for all comparisons). Although both models performed reasonably well, AERMOD performed marginally better under our hybrid approach (onsite wind information combined with other surface characteristics from the
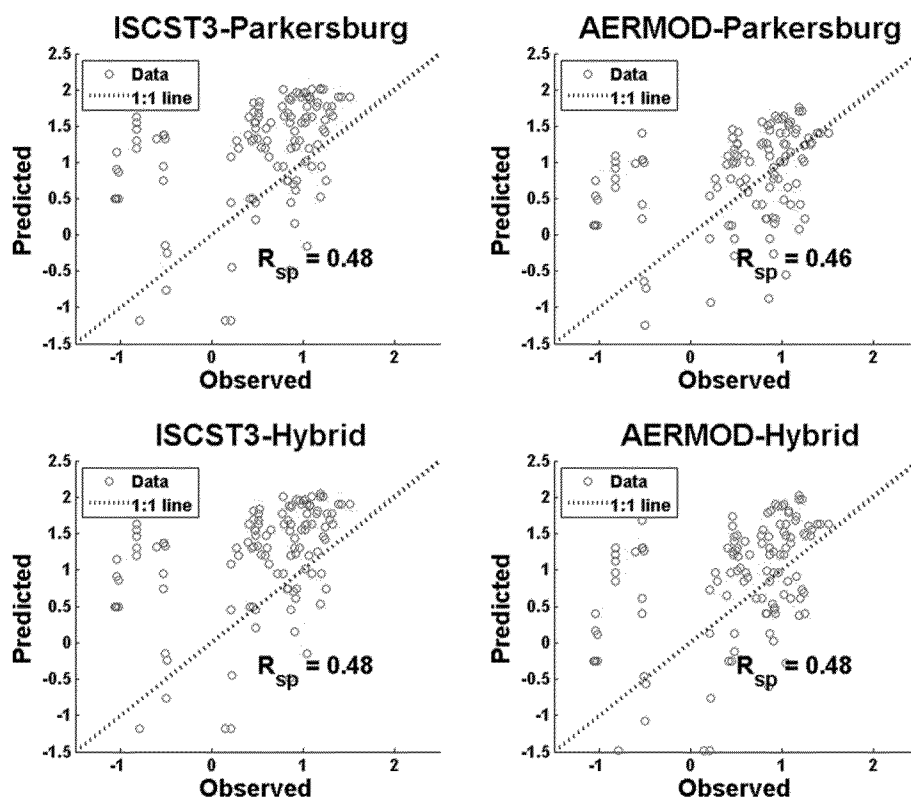

Fig. 3. Linear scatter plots of predicted and observed subsurface (30 cm to groundwater table) soil concentration (mg kg^{-1}). Predicted and observed concentrations are shown as points.

ISCST3-Parkersburg

AERMOD-Parkersburg

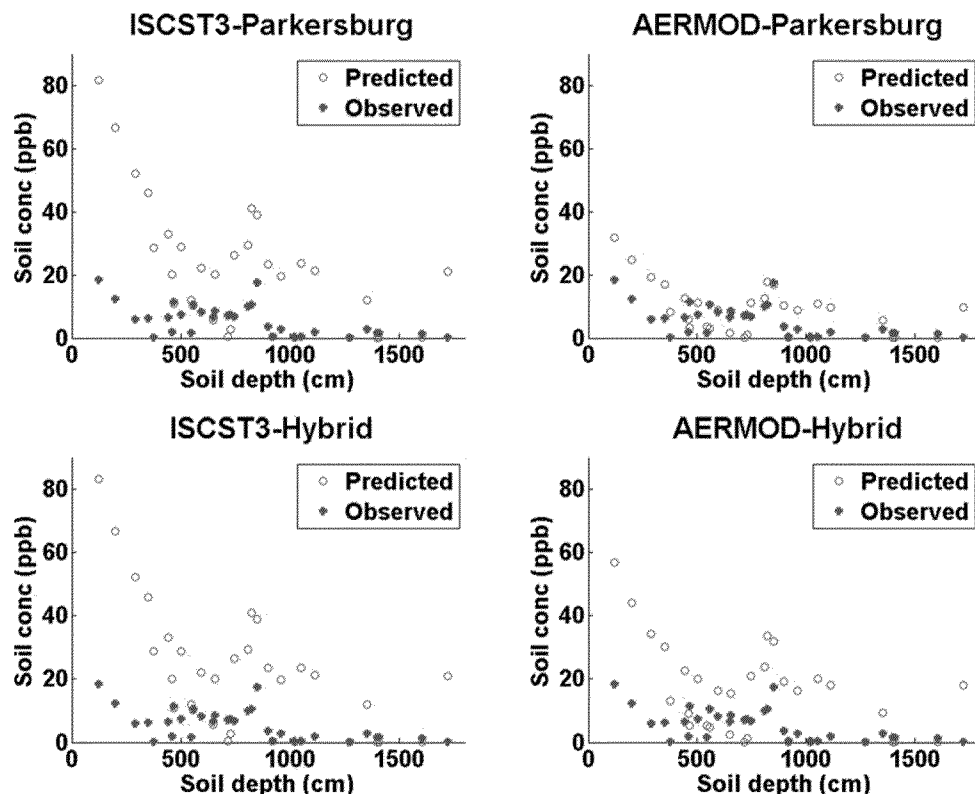## ISCST3-Hybrid

AERMOD-Hybrid

Fig. 4. Scatter plots of cross-sectional subsurface soil concentration prediction profiles by soil depths (cm). Averaged predicted and observed concentrations across sampling locations are shown as filled and blank dots, respectively.

Parkersburg Airport) for handling incomplete meteorological data. We believe the results of this and other similar model comparisons are generally useful to fate and transport modelers, who must choose between reasonable alternative models and incomplete data approaches for any contaminant.

There are more uncertainties for predicting PFOA concentration in subsurface soil compared to surface soil due to limited vertical soil profiles and uncertain chemical properties of PFOA. In addition to vertical soil profile, chemical transport through the vadose zone depends on the soil-water partition coefficient, which is a product of the organic-carbon partitioning coefficient of PFOA and the fraction of organic carbon in soil. Therefore, although the subsurface samples have the advantage of being less influenced by short-term fluctuations in deposition, they are subject to additional model uncertainties and may be complicated by micro-environmental variation in soil characteristics (Hangen et al., 2010). For example, the coefficient of variation for subsurface soil sample concentrations at a similar depth, collected within a radius of 150 meters, was 0.77. In addition, two subsurface soil samples at similar depths (w 3.2 meters) 3 meters apart taken within 6 days of

each other had measured PFOA concentrations that differed by about two orders of magnitudes with little precipitation between samples. This suggests possible measurement errors, sampling errors, or small scale variation in soil characteristics. Laboratory measurement of PFOA is reported to be extremely challenging, suggesting substantial uncertainty regarding both measured soil concentrations and key model parameters. For example, the wide ranges of previously reported estimates of D_{ow} and D_{oc} for the PFOA-PFO[1] pair, described in Section 2.3.3, is a major limitation in using measured soil concentrations to compare different air transport models.

Modeled predictions might be improved if shorter time scale emission rate estimates, particle size data, f_{oc}, and vertical soil types were available. Although DuPont demonstrated that AERMOD predicted air concentrations better than ISCST3 in this region (DuPont, 2007), our results suggest that either model may provide reasonable but slightly over-predictive estimates of soil concentrations, with ISCST3 performing better for surface soil and AERMOD performing marginally better for subsurface soil.

Table 2
Performance of model predictions for subsurface soil (30 cm to groundwater table) concentrations (mg k g[-1]) by different air dispersion models and meteorological data. R_{sp} represents Spearman's correlation rank coefficient and p-value was computed from the McNemar's exact test.

Air model	Meteorological data source	R_{sp}	Under-prediction		Close-approximation		Over-prediction		p-Value
			n	%	n	%	n	%[a]	
ISCST3	Parkersburg Airport	0.48	12	10	20	17	86	73	0.06
AERMOD		0.46	26	22	33	28	59	50	
ISCST3	Hybrid	0.48	12	10	20	17	86	73	0.49
AERMOD		0.48	27	23	25	21	66	56	

[a] Percentage of predictions in each prediction category defined in Model Evaluation section.

Acknowledgments

Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.atmosenv.2012.01.049

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